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## THE ORIGIN OF NITRATES IN CAVERN EARTHS

MUCH interest has been taken in the great caverns of Virginia, Kentucky, and Indiana by tourists, and considerable popular literature has been published, especially in description of Mammoth, Luray, and Wyandot caves. In this literature rather frequent allusion is made to the "nitrates" in cavern earths, and occasionally a theory is advanced to explain their origin. Popular interest is awakened in this question by the large amount of "saltpeter" known to have been taken from Mammoth Cave during the war of 1812, and from similar caverns in Alabama and Georgia during the Civil War for the manufacture of gunpowder.

The origin of this supply of nitrates is commonly ascribed to animal remains, and especially to the excrement of bats. In Mammoth Cave, however, the cavern earth was worked for nitrate for a distance of over five miles from the only opening known which leads to the surface, while bats as a rule go but a short distance from the entrance of the cavern. Again, on account of the antiseptic character of the atmosphere of caves, we would expect, in case the nitrate was derived from bats, to find some animal remains, in the form of their dried bodies, their bones, or their excrement; but organic matter of any kind is rare in cavern earths. The hypothesis ascribing such an origin to the vast stores of nitrates taken from Mammoth and other caverns seems, therefore, inadequate.

Caves in limestone regions are due to the solvent action of water containing carbon dioxide. This process must have been very slow and in most cases unaided by mechanical erosion, thus leaving the insoluble portion of the limestone as a deposit on the floor of the cavern. This residue is known as cavern earth.

From the mode of formation of caves, it is evident that this residue must have been washed perfectly free from all salts.

readily soluble in water by the water which slowly carried away the limestone itself during the formation of the cavern.

Recent progress in bacteriology and agricultural chemistry has thrown much light upon the origin of nitrates in soils by the oxidation of organic matter in the presence of certain bacteria. The surface soil in cavernous regions is usually loose and porous, and consequently favorable both for nitrification of organic nitrogen and for downward percolation of the surface water. It may not be unnatural, then, to ask whether the nitrates in cavern earths may not have originated wholly or in part from nitrification of organic matter at the surface and the subsequent leaching of the nitrates so formed into the caverns. Caves would thereby act merely as receptacles for the surface drainage, and provide an avenue for the return of the percolating water to the atmosphere by evaporation. If the nitrates in caves originated in this way, we would expect to find also in cavern earths such other soluble constituents of soils as must necessarily have been leached out along with the nitrates.

By leaching cavern earths with cold water some material is always extracted. The amount thus washed out is sometimes as much as 13 per cent. of the sample. The following analyses are given of the soluble matter of cavern earths derived by washing the samples with cold water, the figures representing percentages :

Source	Calcium oxide	Sulphuric anhydride	Alkalis	Chlorine	Nitric acid	Ammonia
Mammoth Cave, Ky.	1.06	2.16	1.45	0.28	0.37	0.005
Mammoth Cave, Ky.	3.20	4.57	3.04	1.41	1.36	0.001
Saltpeter Cave, Ind.	2.31	3.30	2.26	0.23	1.88	0.007

From these results it is seen that nitrates form only a small portion of the total soluble material in cavern earths.

A kilo of subsoil over Mammoth Cave was placed in a percolator, and two liters of water charged with carbon-dioxide were added and allowed to stand for a week, with frequent stirrings, when the water was slowly drawn off. The water was then

evaporated in a platinum dish and the residue was analyzed. A sample of cave earth collected as nearly as possible beneath the spot where the sample of subsoil was taken, was also treated in the same way. A sample of bat guano and one of the earth occurring just below the guano were subjected to the same treatment. The results of these several analyses are given in the following table, the figures representing percentages of the sample taken :

	Mammoth Cave		Dixon's Cave	
	Subsoil over Mammoth Cave	Cave earth below	Bat guano	Earth below bat guano
Sulphuric acid, $\text{SO}_3$ . . . . .	0.0054	4.16	0.67	0.031
Lime, $\text{CaO}$ . . . . .	0.0018	2.03	3.34	0.23
Alkalis, $\text{Na}_2\text{O}$ , and $\text{K}_2\text{O}$ . . . . .	0.00288	2.86	0.37	0.26
Phosphoric acid, $\text{P}_2\text{O}_5$ . . . . .	trace	0.0003	0.044	0.0137
Ammonia, $\text{NH}_3$ . . . . .	0.00192	0.011	0.102	0.019
Nitric acid, $\text{N}_2\text{O}_5$ . . . . .	0.0068	0.82	6.016	0.0118

By comparing these analyses it is evident that the soluble material in the cave earths might have been leached from the soil above.

The bat guano forms a thin layer over the floor of Dixon's Cave, and is composed of a mixture of excrement and fuzzy material from the bats' bodies, together with sand and earthy matter from the walls of the cavern. Judging from the above analyses, this layer seems to have acted as an excellent absorbent preventing the further percolation downward of material dissolved from the soil above the cave, since the earth below contains very little soluble material.

But guano was found to contain considerable amounts of salts of phosphoric acid soluble in cold water, while the cavern earths proper contain only traces of these salts. The total percentage of phosphate dissolved out of bat guano by dilute acid was found to be about the same as that derived from cave earth by the same treatment. The following results of analyses of bat guano, taken just as it came from the cave, making no attempt to mechanically separate the sand and earthy matters, and of cave

earth, both from Dixon's Cave, were obtained by igniting the dried samples and then treating them with dilute hydrochloric acid.

		Bat guano	Cave earth
Loss on ignition	- - - - -	32.16	6.02
Insoluble residue	- - - - -	40.65	73.80
Soluble silica, $\text{SiO}_2$	- - - - -	1.03	trace
Calcium oxide, $\text{CaO}$	- - - - -	10.95	7.51
Ferric oxide, $\text{Fe}_2\text{O}_3$	- - - - -	1.20	3.37
Alumina, $\text{Al}_2\text{O}_3$	- - - - -	5.27	2.41
Magnesia, $\text{MgO}$	- - - - -	0.37	0.30
Sulphuric anhydride, $\text{SO}_3$	- - - - -	4.37	2.77
Phosphoric anhydride, $\text{P}_2\text{O}_5$	- - - - -	2.62	2.10
Alkalis and loss	- - - - -	2.38	1.72

This sample of cave earth contained no perceptible organic matter.

It seems from a comparison of these analyses that we cannot prove the presence of animal remains by the total content of phosphoric acid soluble in dilute mineral acids, since a residue from limestone must contain considerable calcium phosphate on account of the insolubility in water of this salt of calcium.

Analyses of the water dripping from the roofs of caves were made, and results were obtained which do not vary markedly from results obtained from analyses of ordinary sub-drainage waters. The following is an analysis of the residue from water which dripped from the roof of Mammoth Cave :

	Milligrams per liter
Silica, $\text{SiO}_2$	12.23
Sulphuric Anhydride, $\text{SO}_3$	15.81
Phosphoric Anhydride, $\text{P}_2\text{O}_5$	trace
Chlorine	2.71
Ferrous Carbonate, $\text{FeCO}_3$	1.02
Calcium Carbonate, $\text{CaCO}_3$	53.61
Magnesium Carbonate, $\text{MgCO}_3$	7.17
Alkalis, $\text{Na}_2\text{O}$ and $\text{K}_2\text{O}$	16.56
Ammonia, $\text{NH}_3$	0.04
Nitric Acid Anhydride, $\text{N}_2\text{O}_5$	5.71

A comparison of the soluble constituents given in this analysis with the soluble material extracted from the cave earth, as

shown in the preceding analyses, points forcibly to the probable origin of these salts in cavern earths.

It was found from analyses of many samples taken from Saltpeter Cave, Indiana, so as to cover practically the whole floor of the cavern from the opening to the end, that nitrates were distributed throughout the entire extent of the dry chamber, irrespective of distance from the entrance. Since bats do not go far inward from the entrance of caves, and since we find no organic matter in cave earth to indicate an animal origin for the nitrate contained therein, it is evident that we cannot regard the nitrates in cavern earths as originating from bat guano.

The conclusion reached from this investigation is that the nitrates in caves were brought in by water percolating through the soils above the caves and were deposited on the floors. Currents of air in and out of the caverns removed the water, and the various salts it previously held in solution were left as an inheritance to the cave earth. A cavern acts, therefore, merely as a receptacle for stopping a portion of the surface drainage. This accumulation of salts occurs only in caverns where the inflow of surface water does not exceed in amount the water removed by evaporation. In wet caves the soluble salts are washed onward with the water bearing them and so are not deposited.

Nitrates found under overhanging cliffs are of a similar origin. Water bearing dissolved nitrates percolates through the soil and finally oozes out at the surface. The water evaporates and leaves behind an incrustation of its soluble materials. The nitrates thus formed under overhanging cliffs remained permanently stored there, being securely protected from rain. They served, along with the nitrates found in the caves of Alabama and Georgia, as a source of saltpeter used by the South during the Civil War for the manufacture of gunpowder.

When vegetable matter is piled up and allowed to decay, an incrustation of potassium nitrate forms on the surface. The vegetable or organic nitrogen has been oxidized to nitric acid. The nitric acid combines with the potash of the plant to form potassium nitrate. The water evaporates from the pile and

leaves its load of nitrate behind as an incrustation on the surface, while water from the interior of the pile works gradually towards the surface to take the place of the water removed by evaporation. Thus the materials soluble in water are slowly brought to the surface and left as a deposit which may be removed mechanically. This is an old method of obtaining saltpeter from manure heaps, and it is even now used to a small extent in Europe. The occurrence of the nitrates in caves as an incrustation on the surface of the cavern earth shows that water has been removed by evaporation in much the same way as from the overhanging cliff and from the compost heap.

We always have nitrogenous matter scattered over the surface of the soil and this decaying vegetation furnishes continuously during its decay a small amount of nitric acid. All nitrates are soluble in water and so are sure to be found in the percolating water. If, then, the percolating water is intercepted and evaporated, the nitrate must be left behind. Nitrates should, therefore, occur in all caves and analyses of the cavern earths of a great number of caves in Indiana and Kentucky demonstrates that the occurrence of nitrates in cavern earths is general. No dry cavern earth was found which did not contain soluble salts of nitric acid, and these salts were distributed uniformly from the entrance to the end of the cavern.

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